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(71) Applicant(s)

Pilkington plc
(Incorporated in the United Kingdom)
Prescot Road, ST HELENS, Merseyside, WA10 3TT,
United Kingdom

Libbey-Owens-Ford Co.
(Incorporated in USA - Delaware)
811 Madison Avenue, Toledo, Ohio 43695,
United States of America

(72) Inventor(s)

Andrew Fraser Simpson
Andrew David McDowell
Douglas M Nelson

(74) Agent and/or Address for Service

Anthony Charles Halliwell
Pilkington plc, Group Patents Department,
Pilkington Technology Centre, Hall Lane, Lathom,
ORMSKIRK, Lancashire, L40 5UF, United Kingdom

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GB 2199848 A **GB 2031756 A** **US 5776603 A**
US 5635287 A **US 5580364 A** **US 5342676 A**
US 5203903 A
WPI Accession no 98-189032 & JP100045434 A

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(54) Abstract Title

Coating glass

(57) A process for the formation of an electrically conductive multi layer coating on the surface of a hot glass substrate by a pyrolytic deposition process is characterised in that the coating comprises at least one layer comprising silicon and oxygen at least one layer of an electrically conductive doped metal oxide and a protective layer of an inorganic material between these layers. Both the layer comprising silicon and oxygen and the layer of a doped metal oxide are deposited in the float bath. The protective layer of an inorganic material is deposited between the two layers. Preferably, the layer comprising silicon and oxygen has less than the stoichiometric amount of oxygen and the layer of doped metal oxide comprises fluorine doped tin oxide. Preferably, the protective layer of an inorganic material comprises silicon dioxide.

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Improvements in Coating Glass

This invention relates to a process for the formation of an electrically conductive coating on a hot glass substrate by a pyrolytic deposition process.

It is known to deposit coatings on to glass substrates by pyrolytic deposition processes. These processes involve a fluid or a solid precursor, usually in a stream of carrier gas, being directed on to a hot glass substrate where it pyrolyses depositing a coating. Chemical vapour deposition (CVD) is one form of pyrolytic deposition wherein the precursor is in the form of a vapour.

CVD of coatings on glass can be carried out on-line during the float glass production process, in which a continuous ribbon of glass is produced on a float bath of molten tin. On-line deposition may be carried out whilst the ribbon of glass advances through the float bath, through the annealing lehr, or through the lehr gap which is the space, open to the air, between the exit of the float bath and the entrance to the annealing lehr. The temperature of the float glass ribbon is highest in the float bath (usually in the range 600-780°C). The float bath atmosphere consists of a flowing non-oxidising gas (usually of nitrogen and hydrogen) so as not to oxidise the molten tin. The temperature of the ribbon in the lehr is usually in the range 580°C - 200°C, and the atmosphere above it is usually air. On line CVD is performed by directing a gaseous mixture containing appropriate precursors on to the surface of the moving glass ribbon through a coater positioned above the ribbon. An example of on-line CVD is provided by US 5,580,364 which discloses a method of producing mirrors comprising depositing, in the float bath, a coating comprising a layer of silicon, an intermediate layer having a refractive index of less than 2, and an outer layer which may be undoped (and therefore non-conductive) tin oxide.

In UK patent specification GB 2 031 756B a process is disclosed for the deposition of a transparent layer of silicon oxynitride.

In UK patent specification GB 2 199 848B a process is described for on-line deposition of a transparent layer comprising silicon, oxygen and carbon on a glass surface at a temperature of 600°C - 750°C by directing a gaseous mixture of a silane, an unsaturated hydrocarbon and carbon dioxide on to the hot glass surface. Such a layer is often referred to as a silicon oxycarbide (or SiCO) layer. The layer blocks the migration of alkali metal ions from the glass into a layer deposited over the layer, and it also suppresses interference colours which can arise in coated glasses which have coatings of a thickness of the order of

the wavelength of light. During deposition the layer incorporates oxygen from the glass but remains chemically reduced in the atmosphere of the float bath i.e. the layer has less than the stoichiometric amount of oxygen. Also described in GB 2 199 848B is the pyrolytic deposition of an infra-red reflecting and electrically conducting layer of fluorine doped tin oxide over the silicon oxycarbide layer, performed on the hot coated glass at the entrance to the lehr in an atmosphere of air. The infra red reflecting layer is deposited on the silicon oxycarbide layer after it has been exposed to the air and thus is no longer reduced.

It would be advantageous to deposit, in the float bath, coatings having electrically conductive doped metal oxide layers (including doped tin oxide layers) and layers comprising silicon and oxygen. However if such coatings are deposited in the bath they are hazy and delaminate from the glass.

The aim of the present invention is to address the above mentioned problem.

The present invention accordingly provides a process for the formation of an electrically conductive coating comprising a multiplicity of layers of material deposited successively on the surface of a hot glass substrate by a pyrolytic deposition process, said coating comprising at least one layer comprising silicon and oxygen and at least one layer of an electrically conductive doped metal oxide, characterised in that both the layer comprising silicon and oxygen and the layer of a doped metal oxide are deposited in the float bath and a protective layer of an inorganic material is deposited between the aforesaid layers.

This is advantageous because coatings produced according to the invention in the float bath are less hazy and less prone to delamination than in the absence of the protective layer.

It will usually be the case that the layer comprising silicon and oxygen is deposited before deposition of the other layers. However, in some cases it may be desirable that the layer comprising silicon and oxygen is deposited after deposition of the other layers.

A layer comprising silicon and oxygen is advantageous because such layers are conveniently deposited by pyrolysis in a range of stoichiometries. The layer comprising silicon and oxygen is usually at least partially reduced, so that the layer comprising silicon and oxygen has less than the stoichiometric amount of oxygen.

The layer comprising silicon and oxygen preferably comprises silicon oxycarbide or silicon oxynitride. A layer of silicon oxynitride may be deposited as described in UK patent specification GB 2 031 756B (in particular as described in Example 1 of GB 2 031 756B or, alternatively, using the source materials for chemical vapour deposition of silicon oxynitride films disclosed in Table E). In a preferred embodiment the layer comprising silicon and

oxygen comprises silicon oxycarbide (SiCO), because this material may be deposited (for example as described in GB 2 199 848 B) in a wide range of stoichiometries which have a correspondingly wide range of refractive indices (from about 3 to about 1.7).

Preferably, the layer comprising silicon and oxygen is deposited by directing a gaseous mixture containing a silane and an unsaturated hydrocarbon onto the hot glass surface.

Preferably, the electrically conductive doped metal oxide comprises doped tin oxide, more preferably the doped tin oxide comprises fluorine doped tin oxide. Alternatively, the doped tin oxide may comprise antimony doped tin oxide.

Electrically conductive doped metal oxides that may also be usefully employed in the present invention include: doped indium oxide, indium tin oxide, doped zinc oxide, doped tungsten oxide and mixtures of these metal oxides.

Preferably the layer of an electrically conductive doped metal oxide has a thickness in the range 100 nm to 400 nm, more preferably the layer of an electrically conductive doped metal oxide has a thickness in the range 150 nm to 350 nm.

The invention is particularly effective wherein the protective layer of an inorganic material comprises a metal oxide, or, preferably, silicon dioxide. This is advantageous because silicon dioxide protects the doped metal oxide layer from reduction (including by loss of oxygen) by the layer comprising silicon and oxygen without itself being significantly reduced. Although less preferred the protective layer may alternatively comprise tantalum oxide, zirconium oxide, aluminium oxide or a non-oxide, for example titanium nitride.

In certain circumstances it may be acceptable if the protective layer contributes to the optical properties of the multilayer coating. However, in a preferred embodiment of the invention, the protective layer of an inorganic material is thin enough to have no significant effect on the optical properties of the coating, especially by reducing the transparency of the coated glass or causing interference colours in reflection or transmission. This is advantageous because the design of the coating is thereby simplified. Thus, preferably the protective layer of an inorganic material has a thickness of below 35 nm, more preferably of below 20 nm and most preferably of below 10 nm.

The float bath preferably has a non-oxidising atmosphere to prevent oxidation of the bath of molten tin. Usually, the float bath has a non-oxidising atmosphere that comprises a gaseous mixture containing hydrogen and nitrogen.

The process is advantageously performed when the hot glass substrate is at a temperature in the range 600°C to 800°C especially at a temperature in the range 600°C to 750°C.

The preferred pyrolytic deposition process is chemical vapour deposition. This is advantageous because particularly good quality coatings may be produced by chemical vapour deposition. The preferred form of chemical vapour deposition (CVD) is laminar flow CVD although turbulent flow CVD may also be used. Other pyrolytic deposition processes may also be suitable including those in which the precursor is in the form of a liquid, especially dispersed as a fine spray (a process often referred to as spray deposition) or in the form of a solid. The pyrolytic deposition process is preferably performed at substantially atmospheric pressure.

In another aspect, the present invention additionally provides a coated glass comprising an electrically conductive coating formed on the surface of a glass substrate said coating comprising at least one layer of silicon oxycarbide or silicon oxynitride and at least one layer of an electrically conductive doped metal oxide, characterised in that the layer of silicon oxycarbide or silicon oxynitride has less than the stoichiometric amount of oxygen and in that a protective layer of metal oxide or silicon dioxide is disposed between the aforesaid layers.

Coated glass produced by the process of the invention is preferably transparent with little or no apparent interference colours in reflection or transmission. Preferably the haze of the coated glass is below 2.5%, more preferably below 1%, and preferably its normal emissivity is below 0.5 more preferably below 0.4.

Coated glass produced according to the present invention has uses in many areas of glass use including as transparent electrically conducting substrates or as a controlled emissivity (heat-reflecting) substrate transparent to visible light.

The invention is illustrated but not limited by the following Examples, in which coatings were applied by laminar flow chemical vapour deposition in the float bath on to a moving ribbon of float glass during the float glass production process. In the Examples three-layer coatings were applied to the glass ribbon.

All gas volumes are measured at standard temperature and pressure. The thickness values quoted for the layers were determined by profilometry using a Dektak profilometer, high resolution scanning electron microscopy and optical modelling of the reflection and transmission spectra of the coated glass. The transmission and reflection properties of the

coated glasses were determined for illuminant D65. The quoted a^* and b^* values of the reflection colour of the glasses refer to the CIE Lab colours. Haze of the coated glasses was measured using a Hazeguard haze meter. Normal emissivity was determined in accordance with ISO 12092: 1994(F).

Examples 1-6

A ribbon of 3 mm thick float glass advancing at a lehr speed of 150 m/hour was coated with a three layer coating as the ribbon advanced over the float bath at a position where the glass temperature was in the range of about 705°C to 730°C. The float bath atmosphere comprised a flowing gaseous mixture of nitrogen and 3% hydrogen.

Layer 1 (the first layer to be deposited on the glass) was a layer of silicon oxycarbide (SiCO). Layer 1 was deposited by causing a gaseous mixture of monosilane (SiH_4 , 2.1 litres/min), carbon dioxide (8 litres/min), ethylene (7.25 litres/min) and nitrogen (10 litres/min) to flow parallel to the glass surface in the direction of movement of the glass using apparatus as described in GB patent specification 1 507 966 with a path of travel of the gaseous mixture over the glass surface of approximately 0.15 m. The glass ribbon was coated across substantially its whole width of approximately 2 m. The refractive index of the SiCO layer was about 1.7 and its thickness about 80 nm.

Layer 2 (the second layer to be deposited) was a layer of silicon dioxide. Layer 2 was deposited by causing a gaseous mixture of monosilane, oxygen, ethylene and nitrogen with flow rates of these gases as described in Table 1 for each of the Examples 1-6 to flow parallel to the glass surface using an oil cooled graphite beam. The path of travel of the gaseous mixture over the glass surface was approximately 0.15 m in the direction of movement of the glass. The glass ribbon was coated along one edge over a width of approximately 10 cm. The thickness of layer 2 varied as the composition and flow rate of the gaseous mixture was varied.

Layer 3 (the third and final layer to be deposited) was a layer of fluorine doped tin oxide. Layer 3 was deposited by causing a gaseous mixture comprising dimethyl tin dichloride (DMT) in flowing nitrogen carrier gas, oxygen (1.2 litres/min), nitrogen (4.3 litres/min), helium 4.3 (litres/min) and hydrofluoric acid (75% solution in water, 0.004 litres/min) to flow parallel to the glass surface using an oil cooled dual flow coater (i.e. gas flow both upstream and downstream along the glass ribbon). The path of travel of the gaseous mixture in the direction of movement of the glass was about 0.15 m and, against the

direction of movement of the glass, was about 0.15 m. DMT was entrained in the flowing nitrogen carrier gas by passing nitrogen at a flow rate of 0.85 litres/min through a bubbler containing DMT. The bubbler was maintained at a temperature of 150°C. The thickness of layer 3 of fluorine doped tin oxide (doped with fluorine from the hydrofluoric acid) was approximately 320 nm.

The properties of the three-layer coating were measured as described above. Values of the thickness of layer 2 (the silica layer), and the haze, normal emissivity, sheet resistance, reflection colour and visible light transmission of the coated glasses are described in Table 2 for each of the Examples 1-6.

Example 7 - 10

These Examples were conducted under the same conditions as Examples 1-6 except that the flow rates and composition of the gaseous mixtures to deposit layer 1 of SiCO and layer 2 of silica were as described in Table 3 for each of the Examples 7-10. The refractive index of the SiCO layer (measured by optical modelling of the spectra and quoted for 500 nm) was about 2.05 in Example 7, 1.88 in Example 8, and 1.73 in Examples 9 and 10. The composition and flow rates of the gaseous mixture for deposition of layer 3 of tin oxide (doped with fluorine from hydrofluoric acid) was as described for Examples 1-6. The thickness of the fluorine doped tin oxide layer (estimated by reflection colour) was about 310 nm and its fluorine content between 0.51 and 0.78% as determined by X-ray fluorescence.

The properties of the three-layer coating were measured as described above. Values of the thicknesses of layer 1 (the SiCO layer) and layer 2 (the silica layer), and the haze, normal emissivity, sheet resistance, reflection colour and visible light transmission of the coated glasses are described in Table 4 for each of the Examples 7-10. The coated glass is coloured in reflection, but a colour suppressed coated glass could be produced by changing the thicknesses and/or refractive indices of the various layers, especially the SiCO layer.

Example 11

A ribbon of 4 mm thick float glass advancing at a lehr speed of 830 m/hour was coated with a three layer coating across substantially its whole width of approximately 3.5 m as the ribbon advanced over the float bath at a position where the glass temperature was

in the range of about 720°C to 740°C. The float bath atmosphere comprised a flowing gaseous mixture of nitrogen and 6% hydrogen.

Layer 1 (the first layer to be deposited on the glass) was a layer of silicon oxycarbide (SiCO). Layer 1 was deposited by causing a gaseous mixture of monosilane (1.5 kg/hr), carbon dioxide (4.5 kg/hr), ethylene (4.5 kg/hr) and nitrogen (3 kg/hr) to flow parallel to the glass surface in the direction of movement of the glass using a uni-directional coater with a path of travel of the gaseous mixture over the glass surface of approximately 0.2m. The refractive index of the SiCO layer was about 1.7 and its thickness about 70 nm.

Layer 2 (the second layer to be deposited) was a layer of silicon dioxide. Layer 2 was deposited at a temperature of about 688 to 693°C by causing a gaseous mixture of monosilane (5 litres/min), oxygen (ratio of 2:1 oxygen to silane), ethylene (ratio of 6:1 ethylene to silane) and made up to a total flow rate of 600 litres/min with nitrogen to flow parallel to the glass surface using an oil cooled dual flow coater (i.e. gas flow both upstream and downstream along the glass ribbon). The coater was cooled by oil at a temperature of 90°C. The path of travel of the gaseous mixture in the direction of movement of the glass was about 0.2 m and against the direction of movement of the glass was about 0.2 m. The thickness of layer 2 varied as the composition and flow rate of the gaseous mixture was varied.

Layer 3 (the third and final layer to be deposited) was a layer of tin oxide deposited by causing a gaseous mixture comprising tin tetrachloride (15 kg/hr), water (2.1 kg/hr), methanol (0.5 litres/hr), nitrogen (about 346 litres/min), helium (about 346 litres/min) and hydrofluoric acid (20% solution in water, 4 kg/hr) (total flow rate of 750 litres/min at a feed temperature of 180°C) to flow parallel to the glass surface using an oil cooled dual flow coater (i.e. gas flow both upstream and downstream along the glass ribbon, oil temperature 180°C). The path of travel of the gaseous mixture in the direction of movement of the glass was about 0.2 m and, against the direction of movement of the glass, was about 0.2 m. The thickness of layer 3 of fluorine doped tin oxide (doped with fluorine from hydrofluoric acid) was approximately 160 nm.

The coated glass had a haze of 3.5%.

Comparative Examples

Comparative Example A was produced under the same conditions as Example 1 except that layer 2 (the silica layer) was not deposited.

Comparative Example B was produced under the same conditions as Example 9, except that layer 2 (the silica layer) was not deposited.

Comparative Example C was produced under the same conditions as Example 7 except that layer 1 (the SiCO layer) was not deposited.

Comparative Example D was produced under the same conditions as Example 11 except that layer 2 (the silica layer) was not deposited.

The properties of the coatings were measured as described above. Values of the thickness of layer 2 (the silica layer) for Comparative Example C, and the haze, normal emissivity, sheet resistance, reflection colour and visible light transmission of the coated glasses are described in Table 5 for each of the Comparative Examples A-D.

Table 1

Example	Gas Flow Rates			
	SiH ₄ (cm ³ min ⁻¹)	Oxygen (cm ³ min ⁻¹)	Ethylene (cm ³ min ⁻¹)	Nitrogen (cm ³ min ⁻¹)
1	10	20	60	8,000
2	20	40	120	8,000
3	30	60	180	8,000
4	40	80	240	8,000
5	50	100	300	8,000
6	10	20	120	8,000

Table 2

Example	Thickness of Layer 2 (silica layer) (nm)	Haze (%)	Normal Emissivity	Sheet resistance (Ω /square)	Reflection Colour D65		Transmission Y D65(%)
					a*	b*	
1	8	1.2	0.21	30.5	-3.5	1.8	80.7
2	18	1.7	0.22	32.5	1.7	0.4	80.3
3	22	1.4	0.21	36.4	11	-7.7	80.6
4	29	2.2	0.20	39.7	12	-13.1	80.2
5	33	2.3	0.20	44.2	2.6	-10.6	80.2
6	6	1	0.23	39.9	-5.1	3	80.5

Table 3

Example	Gas flow Rates							
	Layer 1 (litre/min)				Layer 2 (cm ³ min ⁻¹)			
	SiH ₄	CO ₂	C ₂ H ₄	N ₂	SiH ₄	O ₂	C ₂ H ₄	N ₂
7	1.6	4	5	20	50	100	300	8,000
8	1.6	5	6.5	20	50	100	300	8,000
9	1.6	8	7.25	20	50	100	300	8,000
10	1.6	8	7.25	20	25	50	150	8,000

Table 4

Example	Thickness of Layer 2 (silica layer) (nm)	Thickness of Layer 1 (SiCO layer) (nm)	Haze %	Normal Emissivity	Sheet Resistance (Ω/square)	Reflection Colour D65		Transmission Y. D65 (%)
						a*	b*	
7	Not measured	Not measured	1.1	0.18	21.4	-28.6	5.7	73.9
8	35.5	Not measured	1.7	0.15	24.2	-21.2	6.3	77
9	24	46	1.1	0.18	22.4	-16.0	2.3	78.8
10	33	46	0.6	0.22	32.7	14.4	-7.4	81.6

Table 5

Comparative Example	Thickness of Layer 2 (silica layer) (nm)	Haze (%)	Normal Emissivity	Sheet resistance (Ω/square)	Reflection Colour D65		Transmission Y D65(%)
					a*	b*	
A	-	3.6	0.26	140	15.4	-7.3	68.4
B	-	4	0.54	157	-24.2	6.0	67.4
C	37	2.0	0.15	14.8	-12.3	9.8	78.6
D	-	High	-	-	-	-	-

Claims

1. A process for the formation of an electrically conductive coating comprising a multiplicity of layers of material deposited successively on the surface of a hot glass substrate by a pyrolytic deposition process, said coating comprising at least one layer comprising silicon and oxygen and at least one layer of an electrically conductive doped metal oxide, characterised in that both the layer comprising silicon and oxygen and the layer of a doped metal oxide are deposited in the float bath and a protective layer of an inorganic material is deposited between the aforesaid layers.
2. A process as claimed in claim 1 wherein the layer comprising silicon and oxygen is deposited before deposition of the other layers.
3. A process as claimed in claim 1 wherein the layer comprising silicon and oxygen is deposited after deposition of the other layers.
4. A process as claimed in any one of the preceding claims wherein the layer comprising silicon and oxygen has less than the stoichiometric amount of oxygen.
5. A process as claimed in any one of the preceding claims wherein the layer comprising silicon and oxygen comprises silicon oxycarbide or silicon oxynitride.
6. A process as claimed in any one of the preceding claims wherein the layer comprising silicon and oxygen is deposited by directing a gaseous mixture containing a silane and an unsaturated hydrocarbon onto the hot glass surface.
7. A process as claimed in any one of the preceding claims wherein the electrically conductive doped metal oxide comprises doped tin oxide.
8. A process as claimed in claim 7 wherein doped tin oxide comprises fluorine doped tin oxide.

9. A process as claimed in any one of the preceding claims wherein the layer of an electrically conductive doped metal oxide has a thickness in the range 100 nm to 400 nm.
10. A process as claimed in claim 9 wherein the layer of an electrically conductive doped metal oxide has a thickness in the range 150 nm to 350 nm.
11. A process as claimed in any one of the preceding claims wherein the protective layer of an inorganic material comprises a metal oxide.
12. A process as claimed in any one of claims 1 to 10 wherein the protective layer of an inorganic material comprises silicon dioxide.
13. A process as claimed in any one of the preceding claims wherein the protective layer of an inorganic material has a thickness of below 35 nm.
14. A process as claimed in claim 13 wherein the protective layer of an inorganic material has a thickness of below 20 nm.
15. A process as claimed in claims 14 wherein the protective layer of an inorganic material has a thickness of below 10 nm.
16. A process as claimed in any one of the preceding claims wherein the float bath has a non-oxidising atmosphere that comprises a gaseous mixture containing hydrogen and nitrogen.
17. A process as claimed in any one of the preceding claims wherein the hot glass substrate is at a temperature in the range 600°C to 800°C.
18. A process as claimed in claim 17 wherein the hot glass substrate is at a temperature in the range 600°C to 750°C.
19. A process as claimed in any one of the preceding claims wherein the pyrolytic deposition process is chemical vapour deposition.

20. A coated glass produced by a process as claimed in any one of the preceding claims.
21. A coated glass comprising an electrically conductive coating formed on the surface of a glass substrate said coating comprising at least one layer of silicon oxycarbide or silicon oxynitride and at least one layer of a doped metal oxide, characterised in that the layer of silicon oxycarbide or silicon oxynitride has less than the stoichiometric amount of oxygen and in that a protective layer of metal oxide or silicon dioxide is disposed between the aforesaid layers.
22. A coated glass as claimed in either claim 20 or claim 21 wherein the haze of the coated glass is below 2.5%.
23. A coated glass as claimed in claim 22 wherein the haze of the coated glass is below 1%.
24. A process for the formation of a coating on the surface of a hot glass substrate as claimed in claim 1 and substantially as herein described with particular reference to the Examples 1 to 11.



INVESTOR IN PEOPLE

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Claims searched: 1-24

Examiner: Pete Beddoe
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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

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Int Cl (Ed.7): C03C (17/245, 17/34)

Other: Online: WPI, EPODOC, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
Y	GB 2199848 A (PILKINGTON) see esp p5 lines 12-20 & exs	1 at least
Y	GB 2031756 A (GORDON) see esp p6 lines 58-63 & p7 lines 48-52	1 at least
X	US 5776603 (SAINT-GOBAIN) see esp exs	1 at least
Y	US 5635287 (SAINT-GOBAIN) see esp exs	1 at least
Y	US 5580364 (LIBBEY-OWENS) see esp col3 lines 8-31; exs 1,2,3 & Table 1	1 at least
X	US 5342676 (SAINT-GOBAIN) see esp col6 lines 14-19, ex 4 (col7 lines 28-35) & ex 6 (col8 lines 3-5)	1 at least
Y	US 5203903 (GLAVERBEL) see esp ex 1	1 at least
X	WPI Accession no 98-189032 & JP 10045434 A (GENERAL) see abstract	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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